Cement and Concrete Research 41 (2011) 1177–1184

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Incorporation of trace elements in Portland cement clinker: Thresholds limits for Cu, Ni, Sn or Zn

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ARTICLE INFO

Article history:
Received 22 December 2010
Accepted 20 July 2011

Keywords:
Threshold limit
Heavy Metals (D)
Portland Cement (D)
Clinker (D)

ABSTRACT

This paper aims at defining precisely, the threshold limits for several trace elements (Cu, Ni, Sn or Zn) which correspond to the maximum amount that could be incorporated into a standard clinker whilst reaching the limit of solid solution of its four major phases (C_3S, C_2S, C_3A and C_4AF). These threshold limits were investigated through laboratory synthesised clinkers that were mainly studied by X-ray Diffraction and Scanning Electron Microscopy. The reference clinker was close to a typical Portland clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF). The threshold limits for Cu, Ni, Zn and Sn are quite high with respect to the current contents in clinker and were respectively equal to 0.35, 0.5, 0.7 and 1 wt.%. It appeared that beyond the defined threshold limits, trace elements had different behaviours. Ni was associated with Mg as a magnesium nickel oxide ($MgNiO_2$) and Sn reacted with lime to form a calcium stannate (Ca_2SnO_4). Cu changed the crystallisation process and affected therefore the formation of C_3S. Indeed a high content of Cu in clinker led to the decomposition of C_3S into C_2S and of free lime. Zn, in turn, affected the formation of C_3A. $Ca_6Zn_3Al_4O_{15}$ was formed whilst a tremendous reduction of C_3A content was identified. The reactivity of cements made with the clinkers at the threshold limits was followed by calorimetry and compressive strength measurements on cement paste. The results revealed that the doped cements were at least as reactive as the reference cement.

1. Introduction

In recent years, sustainable development and natural resources preservation have become global issues. The cement industry, which is known to consume a large quantity of raw material and energy, has integrated these issues to its development policy by promoting industrial wastes as raw materials and fuels in replacement for traditional materials used during the manufacturing process. The sources of alternative raw material are varied and provide the necessary ingredients for the raw mix (Ca, Si, Al and Fe). Blast furnace slag, fly ash, iron ores, mill scale, foundry sand, for example, can be used as alternative raw materials [1,2]. In addition, many plants use alternative fuels like scrap tyres, plastics, waste oils as substitutes for coal and petroleum coke [1,2]. However these wastes contain trace elements that could be incorporated into the cement phases during the clinkering process and could affect the technical and environmental properties of cement. Currently, the content of trace elements in Ordinary Portland Cement (OPC) is quite low (Table 1). Consequently, no effect on technical and environmental cement properties has been observed.

Although, the reuse of materials in cement manufacturing is currently considered as beneficial, cautions must be taken. Indeed, during the last decade, wastes valorisation has become a common practice in cement industry and the trace elements content in cement has increased [2].

Many studies have been conducted on the effect of trace elements in cement [3–12]. A literature review, detailed later in Section 2, shows that the data are still incomplete and often contradictory. A very important data, referred here as threshold limit, is still missing for numerous trace elements.

Before defining in more details the concept of threshold limit, it is necessary to recall some general notions of thermodynamics about the incorporation of trace elements into the clinker phases.

As described by Herfort et al. [13], the mechanism of action of the trace elements can be divided in two main steps depending on the amount of these elements.

- At low concentration, trace elements enter into the structure of the initial phases of the clinker (C_3S, C_2S, C_3A and C_4AF) and form different phase assemblages of solid solutions (C_3Sss, C_2Sss, C_3Ass, C_4AFss). At this step, no new phases are detected and the free energy (ΔG_{mix}) of these phase assemblages is lower than the combined free energy of the initial phases and the trace elements. The free energy of each phase could be defined as $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$. ΔH_{mix} corresponds to the enthalpy of mixing and is due to

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doi:10.1016/j.cemconres.2011.07.006

Table 1
Average content in trace element in current Portland cement. [2].

Trace element	Average concentration in OPC, wt.%
As	0.0008
Cr	0.0068
Cu	0.0038
Ni	0.0045
Pb	0.0027
Sn	0.0003
V	0.0074
Zn	0.0164

the distortion of the crystal lattice. ΔS_{mix}, in turn, corresponds to the entropy of mixing and is responsible to the decrease in free energy. It should be noted that the effect on ΔH_{mix} and ΔS_{mix} can't be separated.

- When the content in trace elements increases, the presence of new phases is detected (by XRD for example). New phase assemblages must be considered compared to the original one. For example:

$$C_3Sss, C_2Sss, C_3Ass, C_4AFss \text{ and a X phase.}$$

Consequently, the threshold limit can be defined as the point between these two mechanisms and corresponds to the limit of solid solution of the clinker phases.

The determination of the threshold limit can be investigated by two different ways:

- The first one is to wait for a cement manufacturer's problem induced by trace elements and then investigate the threshold limit. Indeed, the use of animal meal as alternative fuel in cement manufacture induced in the past a decomposition of C_3S into C_2S and free lime. Following this problem, Girod-Labianca et al. [14] studied the effect of phosphorous on the main clinker phase and defined a threshold limit for P_2O_5 on clinker. It corresponds to the maximum amount of P_2O_5 that could be incorporated into clinker before the detection of $\alpha' C_2S$. It is equal to 0.5 wt.%.
- The second way is to investigate the threshold limit for trace elements in order to prevent cement quality problems. The present work fits into this approach.

To prevent the same problems as those encountered for phosphorous, we choose to investigate the concept of threshold limits for four trace elements i.e. Cu, Ni, Sn or Zn that could possibly have deleterious effects if their content continues to increase in cement.

Firstly, we determined for a standard laboratory-made clinker the threshold limit of these four trace elements incorporated at different levels in the same specific clinker of a Portland cement and secondly the reactivity of cements made with the clinkers at the threshold limits. The effect of the trace elements on the clinker phases was investigated by X-ray Diffraction (XRD) and by Scanning Electron Microscopy (SEM). The reactivity of the doped cement paste was followed by isothermal calorimetry and also by the measurements of the compressive strength.

2. Literature review

The four trace elements studied in this paper, were chosen by virtue of their frequent presence in raw materials and fuels. As mentioned previously in the Introduction, a large number of studies have been conducted on the effect of trace elements in cement. Three main research topics were investigated:

- the effect on the stability and the reactivity of pure clinker phases [3–5],
- the effect on clinker particularly on the incorporation rate, the burnability and the sintering process and the mineralogy of the clinker phases [6–9],
- the immobilisation of trace elements in cementitious materials [10–12].

Here, a literature review focused on Cu, Ni, Zn and Sn is presented.

Cu can be found in large quantities in dust, galvanic sludge, iron industry wastes, iron ore and fly ash [2,15]. Although their melting points are respectively equal to 1326 and 1235 °C, CuO and Cu_2O are largely incorporated into the clinker phases [15]. In cement clinkering, CuO is known to act as mineraliser [16,17] because it decreases the melt temperature considerably (at least by 50 °C) and favours the combination of free lime. In clinker phases, Hornain [6] showed that Cu is mainly concentrated in the ferrite phase followed by alite, aluminate phase and belite. Moreover, for high intakes of Cu in clinker, several studies revealed the presence of a new phase rich in Cu and containing CaO [18,19]. The incorporation of Cu into the clinker seemed to have different effects on the grindability. For example, Tsivilis et al. [20] showed that an addition of 2 wt.% Cu had little effect on the grindability whereas Bhatty [9] showed that only 0.25 wt.% Cu decreased the grindability of the clinker. The effect of Cu on cement hydration was also studied [8,9,21]. The results indicated that Cu delayed the hydration particularly during the first days and affected in consequence the early compressive strength which decreased. After 28 days of hydration, the compressive strengths were slightly lower but the difference observed was less important than that observed for the early ages.

Finally, soluble salts of copper were known to delay cement hydration [22–25] and thus to decrease the early compressive strength. Kakali et al. [21] explained this delay in cement hydration by the formation of $Cu(OH)_2$ which covers the calcium silicates during the early ages.

Ni, like Cu, comes from wastes generated by iron industry, iron ore and fly ash [2,16]. In the kiln, Ni is quite non-volatile [15]. Ni is preferentially concentrated in ferrite phase, followed by alite, aluminate phase and belite [6]. For clinkers containing Mg, Ni is mainly incorporated into periclase [10]. Reports on the effect of Ni on the grindability of the clinker are conflicting. Bhatty [9] showed that 0.5 wt.% Ni introduced into clinker decreased the grindability. In contrast, Tsivilis et al. [20] indicated that 2 wt.% Ni did not affect the grindability of clinker. During the hydration, Ni seemed to have little effect on cement hydration and did not modify the compressive strength [9,30]. Stephan et al. [30] showed that even 2.5 wt.% Ni did not affect the cement hydration and its mechanical properties.

Soluble salts of nickel had different effects on cement hydration. For example, Miller [22] showed that soluble salts of Ni could act as accelerators and give high early strengths. Recently Gineys et al. [25] showed that Ni added as nitrate salt had little effect on cement hydration.

Zn can be found in a variety of sources. Secondary fuels like tyres, rubber and metallurgical slags contain a large part of Zn [2]. ZnO is easily incorporated into clinker [26]. In cement clinkering, Zn improves the formation of clinker by decreasing the clinkering temperature and favours the combination of free lime between 1000 and 1100 °C. The distribution of zinc into clinker phases is very contradictory. Knöefel [26], for example, showed that zinc is half concentrated into silicates and the remaining half into ferrite phase. In contrast, Hornain [6] showed that Zn was preferentially present in ferrite followed by alite, aluminate phase and belite. This result was in accordance with the studies of Bolio Arcéo et al. [27] and Barbarulo et al. [28]. In addition, they showed that a new phase, identified as $Ca_6Zn_3Al_4O_{15}$, was present when high intakes of Zn (>1 wt.%) were incorporated into clinkers. Boikova [29] showed that increasing additions of Zn modify the symmetry of C_3S from triclinic to rhombohedral. The incorporation of Zn into the clinker seems to have different effect on the grindability. For example, Bhatty [9] showed that 0.5% Zn had little effect on the grindability of the clinker whereas Tsivilis et al. [20] reported that an addition of 2 wt.% Zn induced a decrease on the grindability of the clinker. The effect of Zn during hydration was also studied. It induced a delay on cement hydration and reduced the early compressive strength for a Zn content higher than 1 wt.% in clinker [30].

Soluble salts of zinc are well-known to induce an important retarding effect on cement hydration and consequently affect the early compressive strength generated by OPC [10,25,30–32]. This phenomenon had been widely studied, and several hypotheses were made. The first hypothesis [33] dealt with the formation of a heavy metal hydroxide on the surface of the anhydrous cement grains. Recently, Week et al. [34] proposed another mechanism based on the conversion of a metal hydroxide to metal hydroxyl species. This reaction consumes calcium and hydroxide ions and reduces the supersaturation of the solution with respect to C–S–H and $Ca(OH)_2$ and, hence, delays this precipitation.

Sn is present in trace amount in fly ash, refuse derived fuels (RDF), plastics, and pesticides [35]. It is also found in paints, as a substitute for lead and cadmium compounds considered as dangerous to human health [36] and as a biocide (TBT: tributyltin) in antifouling paints [37]. Contrary to the other trace elements selected, just a few studies dealt with the effect of tin on the clinkerisation process and/or hydration. Recently Kolovos et al. [18] studied the effect of high intakes of Sn on clinker. The study showed that little Sn was incorporated into C_3S and no Sn was detected in C_2S. In contrast, the analyses revealed that Sn was mainly incorporated in the interstitial matrix. Moreover needle like crystals with a high content Ca had been observed by SEM.

Hill et al. [38] have studied the effect of tin chlorides introduced during mixing and showed that they induced a delay on cement hydration and lead to the formation of two additional hydration products i.e. a Friedel's salt and a calcium hydro-stannate ($CaSn(OH)_6$).

Despite the numerous investigations undertaken on these four trace elements, some data are still missing. This is particularly true for the concept of threshold limits that is defined as the maximum amount of trace element that could be incorporated into clinker whilst reaching the limit solution of its four major phases.

3. Materials and methods

3.1. Materials

Clinkers were prepared by mixing analytical grade reagents of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, MgO and K_2O. First, a reference clinker with a composition close to that of an average clinker of Ordinary Portland Cement (OPC) was synthesised in the laboratory. Table 2 shows the chemical and the mineralogical compositions (according to the Bogue formula) of the reference clinker after sintering. To prepare the doped clinkers, trace elements were introduced into the raw meal in the form of oxide (CuO, NiO, SnO_2 or ZnO). The raw mixes were homogenised and pressed at 5 kN into pellets (height = 23 mm, diameter = 40 mm) to obtain a more regular clinkering process. Pellets were placed in alumina crucible and fired up to 1450 °C a rate of 10 °C/min. After 45 min of burning to the clinkering temperature, the clinker was slowly cooled in the furnace to obtain larger calcium aluminates crystals, in order to facilitate their analysis with SEM equipped with an energy dispersive X-ray spectrometer (EDS). The free lime content of the reference clinker was determined according to the standard ethylene glycol method [39] and was equal to 0.35 wt.%. The raw mix and burning conditions were unchanged for the reference and the doped clinkers. The clinker was ground to a Blaine specific surface between 4500 and 5000 cm²/g. Finally, cement was obtained by mixing the clinker with pure gypsum (<40 μm) in order to reach 3.3% SO_3.

Table 2
Chemical and mineral composition (%w/w) of the reference cement.

Chemical composition	
CaO	68.07
SiO_2	22.98
Al_2O_3	4.73
Fe_2O_3	2.72
MgO	0.80
K_2O	0.69
Mineral composition (according to Bogue formula)	
C_3S	65
C_2S	18
C_3A	8
C_4AF	8

3.2. Methods

The chemical composition of clinker was checked by X-ray fluorescence. For clarity, all the doping concentrations are expressed as trace element weight percentage present in clinker.

The mineralogy of the clinkers was studied by the means of XRD. A Bruker D8 with Co Kα radiation (1.78) was used. The X-ray patterns were acquired in the 2θ (5–100°) with a step of 0.019° and 3 s per step.

The chemical composition of the clinker phases was investigated on polished sections with a Hitachi S-4300SE/N SEM operating in backscattered electron mode (20 keV) and equipped with a Thermo Scientific Ultradry EDS. To make the polished section, a piece of clinker was vacuum impregnated in epoxy resin and then polished with ethanol to avoid reaction with water. Finally the samples were carbon coated before observation.

The reactivity of the cements was determined by isothermal calorimetry measurements performed at 20 °C. 5 g of cement and 2.5 g of water previously stored at 20 °C were mixed manually for few seconds directly outside the calorimeter in cells that were then placed inside the calorimeter. The calorimeter used was a home-made calorimeter using fluxmeters that allowed the calorimeter to equilibrate in less than 2 min after the cells were placed in it. Thus, it was possible to record the heat flux released till the hydration beginning even if the mixing of the cement paste was performed outside the calorimeter.

Due to the limited quantities of the clinker produced in laboratory (about 100 g), the compressive strength was determined on small cylinders (height = 12 mm, diameter = 6 mm) made by cement paste with a water/cement ratio (w/c) of 0.45 according to a method derived from Perez [40–42]. Cement and water were manually mixed for 3 min. The paste was loaded into polytetrafluoroethylene (PTFE) moulds. The filling of the moulds was performed in two steps on a vibration table. The moulds were kept for 24 h at 100% relative humidity and 20 °C. The paste cylinders were demoulded after 24 h and curing was continued at 100% relative humidity and 20 °C. The compressive strength was measured on 5 samples after 2, 7 and 28 days. The tests were performed at a constant stress of 0.3 MPa/s using a uniaxial press.

4. Results and discussion

The first part of this section will be devoted to determining the respective threshold limits for Cu, Ni, Sn or Zn by XRD and MEB. Then, the reactivity of the doped cement paste was investigated by isothermal calorimetry and also by the measurements of the compressive strength.

4.1. Threshold limit values

To determine the threshold limits, different concentrations of the selected trace elements were incorporated in the raw-mix. The resulting clinkers were analysed by XRD and compared to the reference.

The XRD analysis conducted on the reference showed that the major crystalline phases of OPC (C_3S, C_2S (β), C_3A and C_4AF) were present in clinker whereas no CaO was identified. The comparison with the XRD patterns of doped clinkers (Figs. 1A, 2A, 3A, 4A) revealed that the addition of the trace elements in clinker led to different effects on the clinker phases. Indeed, two different behaviours were observed. For Ni and Sn, the chemical composition of the phase assemblages (C_3Sss, C_2Sss, C_3Ass, C_4AFss) remained similar and their quantity was not significantly different from that present in the standard clinker. Cu and Zn, in contrast, strongly modified the phase assemblages of clinker.

Here, the threshold limit is defined as the maximum amount in trace elements that could be incorporated into a standard clinker whilst reaching the limit of solution of its four major phases. The threshold limit is reached when a new phase and/or a decrease in the initial clinker phases is detected by XRD.

4.1.1. Trace elements preserving the phase assemblages

The XRD patterns of clinkers respectively doped with Ni and Sn (Figs. 1A and 2A) revealed that the incorporation of high contents in these two trace elements led to the formation of $MgNiO_2$ and Ca_2SnO_4. To validate these results, clinkers respectively doped with a high Ni (3.6 wt.%) and Sn (4.8 wt.%) content were analysed by the means of SEM-EDS. Figs. 1B and 2B showed that Ni and Sn were primarily concentrated in the interstitial phase respectively as $MgNiO_2$ and Ca_2SnO_4. These results are in accordance with previous work as mentioned in Section 2. Indeed, Stephan et al. [7] and Kolovos et al. [20] had previously described the same effects of Ni and Sn on the clinker phases.

Here, the threshold limits for Ni and Sn will be respectively reached when $MgNiO_2$ and Ca_2SnO_4 appeared in clinker. The observations of XRD patterns (Figs. 1A and 2A) indicated that $MgNiO_2$ appeared when 0.5 wt.% Ni was incorporated into the raw materials of the clinker. On the other hand, Ca_2SnO_4 was observed when the Sn content exceeded 1 wt.%. In addition, the formation of Ca_2SnO_4 reduces the amount of Ca available to form calcium silicates and particularly C_3S which seemed to decrease beyond the threshold limit.

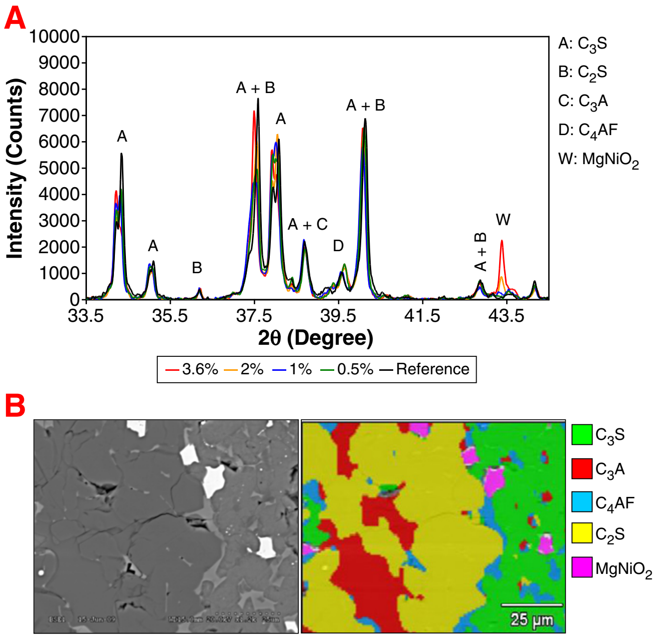

Fig. 1. A) XRD patterns of clinkers doped with different Ni concentrations; B) SEM Micrograph (left) and elemental X-ray images (right) of clinkers doped with 3.6 wt.% Ni.

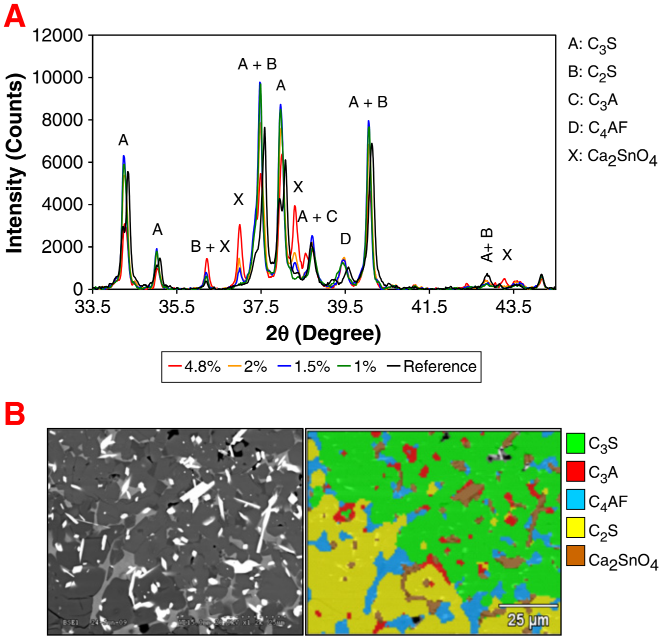

Fig. 2. A) XRD patterns of clinkers doped with different Sn concentrations; B) SEM Micrograph (left) and elemental X-ray images (right) of clinkers doped with 4.8 wt.% Sn.

4.1.2. Trace elements modifying the phase assemblages

The XRD patterns of clinkers respectively doped with Cu and Zn (Figs. 3A and 4A) revealed that the incorporation of high contents of one of these two trace elements led to a modification on the stability of clinkers phases. However, these trace elements did not affect the same phases of clinker.

First, Cu seemed to change the crystallisation process and affected the formation of calcium silicates and particularly that of C_3S. A

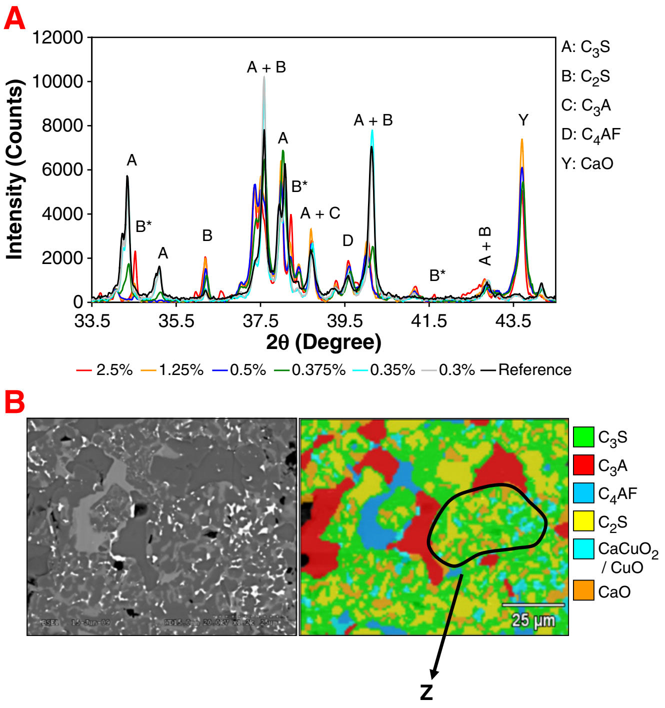

Fig. 3. A) XRD patterns of clinkers doped with different Cu concentrations; B) SEM Micrograph (left) and elemental X-ray images (right) of clinkers doped with 2.5 wt.% Cu.

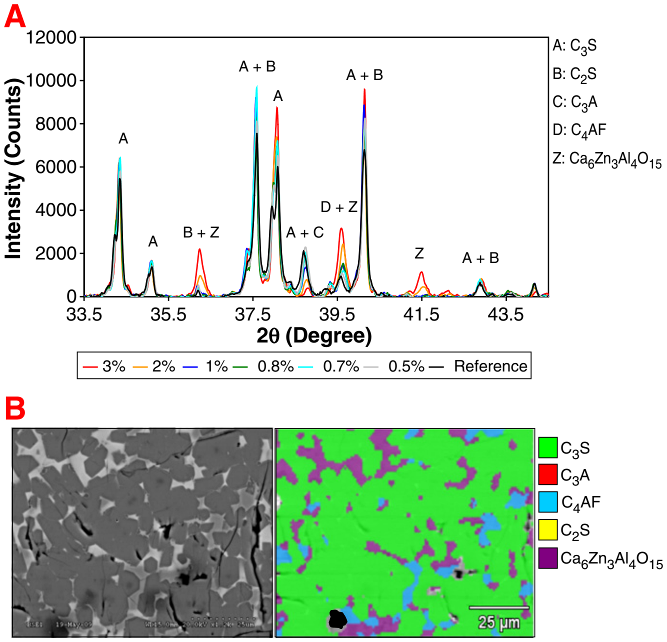

Fig. 4. A) XRD patterns of clinkers doped with different Zn concentrations; B) SEM Micrograph (left) and elemental X-ray images (right) of clinkers doped with 3.5 wt.% Zn.

decomposition of C_3S to C_2S and free lime were observed in the presence of high contents of Cu in clinker (Fig. 3A). In contrast, Zn seemed to react preferentially with alumina and consequently modified the stability of C_3A. A high content of Zn incorporated in clinker induced a decrease in C_3A content. Moreover, a new compound, identified as $Ca_6Zn_3Al_4O_{15}$ [27,28], was observed (Fig. 4A). SEM analyses were conducted on clinkers respectively doped with a high content of Cu (2.5 wt.%) and Zn (3.5 wt.%) in order to validate the XRD observations. The results obtained were totally in accordance with those of XRD. For Cu, the analyses revealed the presence of areas (identified, for example, as Z in the Fig. 3B) that contained a grain of C_3S doped with Cu that was formed at high temperature which was then decomposed during the cooling process into C_2S and free lime. For Zn (Fig. 4B), $Ca_6Zn_3Al_4O_{15}$ was identified and replaced C_3A in the interstitial phase. The same effect of high intakes of Zn on clinker phases was previously described by Bolio-Arcéo et al. [27,43].

Given these results, the threshold limit for Cu will be associated to a decrease in C_3S content and/or an increase of C_2S and free lime. For Zn, the threshold limit will be reached when a decrease in C_3A content and/or the formation of $Ca_6Zn_3Al_4O_{15}$ was observed.

The observations of XRD pattern (Fig. 3A) indicated that a decrease in C_3S and/or an increase in C_2S and free lime contents appeared when the Cu content incorporated into clinker was greater than 0.35 wt.%. In addition, C_2S γ (identified on Fig. 3A as B*) was detected when Cu concentration exceeded this threshold limit.

For Zn (Fig. 4A), a decrease in C_3A content and/or the formation of $Ca_6Zn_3Al_4O_{15}$ was observed when the Zn content was higher than 0.7 wt.%. This concentration corresponds to its threshold limit. Moreover, for clinkers doped with more than 2 wt.% Zn, C_3A had totally disappeared and was replaced by the new phase previously presented as $Ca_6Zn_3Al_4O_{15}$.

4.1.3. Complementary tests

Results, presented into Section 4.1.2, revealed the presence of γ-C_2S in addition to β-C_2S in clinker doped with a Cu content exceeding its threshold limit. The presence of γ-C_2S in clinker is well-known to be deleterious for cement properties because it is an expansive phase which has an extremely low hydraulic reactivity at ambient temperature. As it is less reactive than β-C_2S, it affects the compressive strength [44]. For this reason, a rapid cooling is usually applied in cement industry at the end of the clinkering process. This process helps to stabilise the clinker phases in their high temperature form and thus avoids, for example, the formation of γ-C_2S. Consequently, it could be expected that the rate of cooling of clinker affects the threshold limit and specially that for Cu.

To verify if the rate of cooling could affect on the threshold limits, clinkers doped with Cu, Ni, Sn or Zn were synthesised and quenched to ambient temperature. The resulting doped clinkers were then analysed.

Tests conducted for Cu indicated that the threshold limit of Cu was, indeed, affected by the rate of cooling. Indeed, a decrease in C_3S and/or an increase in C_2S and free lime content was observed for Cu contents greater than 0.5 wt.% (Fig. 5). In addition, for a Cu content exceeding this new threshold limit, no γ-C_2S was identified. Results, obtained for Ni, Sn and Zn, revealed in contrast that their threshold limits were not affected by a rapid cooling. These results are in accordance with that we expected. Indeed, Cu was the only trace element that affects the C_3S stability when its content exceeds the threshold limit.

The behaviour of Cu recalls that previously observed by Mohan and Glasser [45] for sulphates which significantly accelerate the decomposition of alite on cooling. They suggested that it accelerates the decomposition of alite on cooling by modifying its driving force for decomposition. One might think that it is the same phenomenon encountered for Cu. Consequently, the decomposition on cooling of C_3Sss containing Cu is easier than that of the initial C_3S.

In this first part, we highlighted that the threshold limits determined for Cu, Ni, Sn or Zn are significantly higher than the concentrations currently presents in OPC. They are respectively 50 times higher for Zn, 100 times for Cu and Ni and 600 times for Sn [2]. Consequently, these threshold limits are not yet reached. Moreover, this study revealed that small amounts of Cu in clinker could affect the C_3S stability. This result is important to note given the steady increase on the Cu content in industrial cement.

However, this study raises some questions that deserve to be discussed in more detail.

- First, the determination of the threshold limits depends on the detection method used. Indeed, the absence of a phase does not mean that it is not present but only that its content is below the limit of detection. In this study, the presence and/or the absence of a phase were determined by XRD and no Rietveld quantification method was used. Customary method to determine the detection sensitivity of the dilute phase is to prepare the supernumerary phase and make weighted additions to the standard clinker. To evaluate the detection sensitivity of the new phases formed after the threshold limits, different contents (0.5 and 1 wt.%) in the

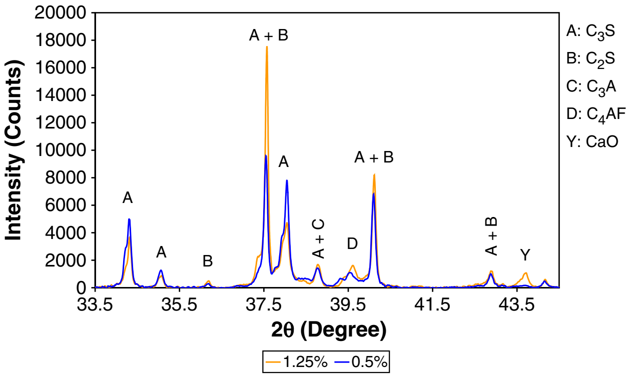

Fig. 5. XRD patterns of clinkers doped with different Cu concentrations — clinkers obtained after a quick cooling at the air.

respective pure phases were added to the reference clinker. Clinkers were analysed by XRD. Results showed that $Ca_6Zn_3Al_4O_{15}$ was not detected by XRD even for a content of 1 wt.%. CaO, in turn, had a limit of detection between 0.5 and 1 wt.%. Finally, the limit of detection of Ca_2SnO_4 was less than 0.5 wt.%. The sensitivity of $MgNiO_2$ could not be performed. Indeed, we were not able to synthesis it as a pure phase in laboratory. However, these limits of detection can be only considered as approximate. Indeed, it is not proved that the XRD behaviour of pure phase added to the reference is the same as when the same phase is produced in situ during the clinkering process.

- Then, the threshold limits defined in this study were expressed for a given clinker of Portland cement. It should be interesting to investigate the validity of these threshold limits for several clinker compositions. The results presented in this paper could give trends concerning the evolution of the threshold limits with the clinker composition. Indeed, it seemed the threshold limit for Cu is affected by the C_3S content of the clinker whilst the threshold limits for Zn and Sn are affected by the interstitial phase content. Concerning Ni, its threshold limit could be linked to the Mg content. A study dealing with the robustness of the threshold limit for Cu, Sn or Zn versus the composition of Portland cement clinker is in progress and will be soon published in a separate paper.
- In addition, it must be taken into account that thresholds limits could be less, if several trace elements are incorporated simultaneously into clinker due to their possible competitive effects.
- The last point deals with the interest to determine mono-elemental threshold limits. Indeed, this approach could be transposed for several applications as the use of by-products in cement production which often contain one trace element at high concentration as the case of phosphorus from animal meal. Moreover, this approach could supply, in the future, a more general investigation of threshold limit in a multi-elemental system.

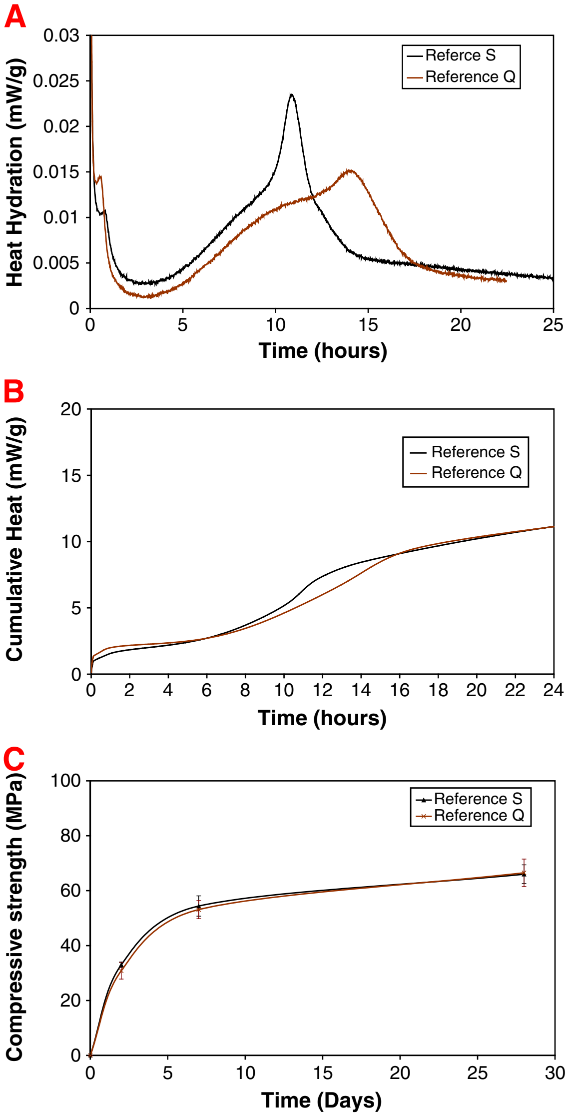

Fig. 6. A) Heat hydration versus time of the S and Q reference cement pastes; B) Cumulated heat at 24 h for the S and Q reference cement pastes; C) Compressive strength obtained after 2, 7 and 28 days of cement paste curing.

4.2. Reactivity of doped cements at the threshold limit

For each threshold limit determined previously in Section 4.1, the reactivity of the corresponding cement was studied and compared to the reference cement. Given that cement hydration is an exothermic process, the observation of heat released can be correlated with the kinetic of hydration of each cement. The reactivity of cement was thus followed by calorimetry. Finally, the compressive strength was measured also on cement paste.

4.2.1. Reactivity of the reference cement

In Section 4.1.3, we highlighted that the threshold limit of Cu was affected by the rate of cooling of the clinker and two threshold limits were therefore determined. To compare the reactivity of these two cements with that of the reference, we needed to verify if the rate of cooling could affect the reactivity of the cement. In consequence, two references produced with a different rate of cooling were prepared and their reactivity was tested. The reference S was obtained after a slow cooling in the furnace whilst the reference Q corresponded to a clinker quenched to ambient temperature. The results of calorimetry and compressive strength are summarised in Fig. 6A, B and C.

Heat flow curves (Fig. 6A) obtained for the two references indicated that the beginning of the major hydration step both occurred after 4 h and was characterised by a main exothermic peak due to the hydration of the anhydrous calcium silicates grains of cement particularly that of C_3S. Then, an additional thermal effect on the descending part of the main peak was observed. It corresponded to the hydration of the remaining part of C_3A and gypsum that had not reacted yet. For the reference S, the second peak occurred at about 10 h whereas it is a little delayed for the reference Q. The C_3A hydration occurred here at about 15 h. The cumulated heat curves (Fig. 6B) indicated, in turn, that the reactivity at early ages (24 h) of the two references was similar.

Finally, the compressive strength for the S and Q references was assessed. These tests were conducted on cement pastes at 2, 7 and 28 days. Fig. 6C showed that the two references produced compressive strengths which were equivalent.

In conclusion, we chose to keep as a unique reference the clinker obtained after a slow cooling to compare the reactivity of the doped cements. Although, a little difference on the C_3A hydration was observed between the two references, we considered that the results of cumulated heat and compressive strength allowed us to consider that they had the same reactivity.

4.2.2. Reactivity of the doped cement

The calorimetry measurements at the threshold limits (Fig. 7A) revealed that the presence of Cu, Ni, Zn and Sn had no effect on cement hydration. Indeed, the major peak of cement hydration appeared at the same time as the reference cement i.e. 4 h. As previously observed in Section 4.2.1, there was a difference in the C_3A behaviour during hydration. Indeed, the presence of Cu, Sn seemed to delay the C_3A hydration. In this paper, we do not discuss this phenomenon. Recall that the aim of this study is to assess the threshold limits for trace elements in a given clinker of Portland cement. In addition, the cumulated heat curves (Fig. 7B), which informed about the reactivity at early ages, seemed to indicate that the amount of heat of hydration released at 24 h by the doped cements was close to the reference.

The tests of compressive strength conducted on cement pastes at 2, 7 and 28 days revealed different behaviours (Fig. 7C). Cement respectively doped with Ni and Zn produced compressive strengths which were close to that of the reference. However, we noted that the values obtained for Ni were more dispersed. This phenomenon could be explained by a less homogeneous cement paste. For cement doped with Sn, the early compressive strengths (2 and 7 days of hydration) were equal to that of the reference whilst it was higher than the reference after 28 days of hydration.

In contrast, the cements doped with Cu (0.35 wt.% and 0.5 wt.%) seemed to develop lower compressive strength at early ages compared to the reference. After 28 days of hydration, the compressive strength measured for cement doped with 0.35 wt.% Cu was close to the reference whereas it was higher than the reference for the cement doped with 0.5 wt.% Cu. Kolovos et al. [8] observed the same phenomenon on early hydration when they have introduced 1 wt.% Cu into clinker. The addition of Cu modified the setting time and particularly the final setting time. They observed a decrease in early compressive strength whereas after 7 days Cu affected it in a positive way. The authors referred to Kakali et al. [21] and explained that the delay observed in early ages is due to the formation of $Cu(OH)_2$ which cover the silicates.

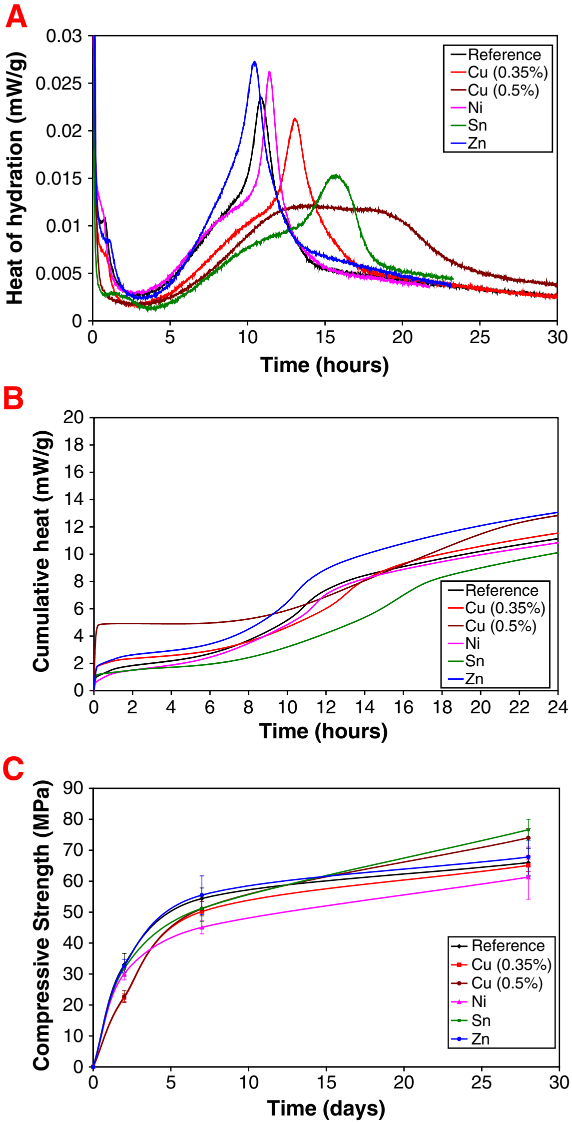

Fig. 7. A) Heat hydration versus time of cement pastes doped with Cu (0.35 wt.% and 0.5 wt.%), Ni (0.5 wt.%), Zn (0.7 wt.%) and Sn (1 wt.%); B) Cumulated heat at 24 h for cement pastes doped with Cu (0.35 wt.% and 0.5 wt.%), Ni (0.5 wt.%), Zn (0.7 wt.%) and Sn (1 wt.%); C) Compressive strength obtained after 2, 7 and 28 days of cement paste curing.

In conclusion, the doped cements seemed to be at least as reactive as the reference. This result is particularly interesting for Zn which is well-known to induce an important delay on cement hydration when they are added during mixing [25]. The incorporation of Zn into clinkers could be a good alternative to the solidification/stabilisation process that is usually used to valorise wastes with a high content in Zn. Recently, we demonstrated that the presence of Zn in the clinker phases did not have an effect on cement hydration even at high levels of Zn (3 wt.%), the cement hydration was not delayed by much as it occurred within the twenty four hours [46].

Moreover, these results highlighted that the criteria used to define the threshold limit as being the maximum amount of trace element that could be incorporated into clinker whilst reaching the limit of solid solution of its four major phases, were correct. The same methodology could thus be applied to any type of Portland cement clinker.

5. Conclusions

The purpose of this work was to define for a given clinker (65% C_3S, 18% C_2S, 8% C_3A and 8% C_4AF) the maximum content for trace elements (Cu, Ni, Sn or Zn) that could be incorporated whilst reaching the limit of solid solution its four major phases referred here as threshold limit. The main conclusions can be summarised as follows:

1. The respective threshold limits for Cu, Ni, Zn and Sn were equal to 0.35, 0.5, 0.7 and 1 wt.%. Except for Cu, these threshold limits are quite high with respect to the current concentrations found in OPC clinker.
2. Threshold limit of Cu is affected by the rate of cooling of the clinker. Indeed, its threshold limit increased from 0.35 to 0.5 wt.% Cu when the clinker is quenched to ambient temperature. This phenomenon could be explained by the fact that Cu accelerates the decomposition of C_3S on cooling by modifying its driving force for decomposition. This phenomenon was only observed in the case of Cu.
3. For a content exceeding their threshold limit, trace elements induced different effects on clinker. Thus, Ni and Sn did not modify the phase assemblages (C_3Sss, C_2Sss, C_3Ass, C_4AFss). Their chemical composition and their quantity were not significantly different from that present in the reference clinker. Their threshold limit was reached when the formation of new compounds respectively $MgNiO_2$ and Ca_2SnO_4 were identified in clinker. In contrast, Cu and Zn strongly modified the phase assemblages of clinker. Indeed, Cu affected the C_3S formation whilst Zn affected C_3A. Their threshold limits were respectively associated with a decrease in C_3S and C_3A contents.
4. Finally, the reactivity of doped cements at the threshold limit was studied by calorimetry and compressive strength measurements. No effect on cement hydration was observed. Only a decrease in early compressive strength (30%) was observed for cement doped with Cu and Sn. However, up to 7 days of hydration, their compressive strength is equal or higher to that of the reference. Consequently, the doped cements seemed to be at least as reactive as the reference.

Acknowledgements

Many thanks to Ghislain Louis for his advice and his help with the SEM and XRD analyses. The authors thank also Damien Betrancourt, Christophe Cappelaere and Guillaume Potier for their technical assistance. Finally, we thank anonymous reviewers for their valuable comments on this paper.

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